FUNDAMENTAL AND EXPLORATORY RESEARCH

Ernest L. Majer

510/486-6709
elmajer @lbl.gov

The Fundamental and Exploratory Research Program (FERP) within ESD covers fundamental earth sciences research conducted in support of the Department of Energy's science mission. This mission includes research in the natural sciences to provide a basis for new and improved energy technologies and for understanding and mitigating the environmental impacts of energy development and use. FERP also includes exploratory research in important new energy and environmental topics conducted under the Laboratory Directed Research and Development (LDRD) program. The scientific insights and breakthroughs achieved in FERP often become the underpinnings for projects that support DOE's applied research and development program offices.

Over the years, the basic earth sciences research program at Berkeley Lab has focused on three broad earth sciences problems:

1. Fundamental studies of chemical and mass transport in geologic media, with special reference to predictive modeling of multiphase, multicomponent, nonisothermal fluid flow in saturated and unsaturated fractured rocks

2. The development of new isotopic techniques for understanding the nature of a broad range of global processes—from the relatively short-term effects of natural fluid migration in the crust to longer-term (i.e., 10–20 thousand years) global climate variations

3. Fundamental studies in the propagation of seismic/acoustic and broadband electromagnetic waves through geologic media, with emphasis on new computational techniques for high-resolution imaging of near-surface and crustal structures (such as possible fracture flow paths) and for inferring the types of fluids present in pores and fractures

Results from these research endeavors have had a major impact on applied energy, carbon management/climate change, environmental, and radioactive waste management programs. Current research projects are briefly described here.

CHEMICAL AND MASS TRANSPORT INVESTIGATIONS

Current research in this area is focused on nanoparticle and colloid transport in unsaturated porous media and rock fractures, chemical transport in structured porous media, unsaturated fast flow in fractured rock, and production and evaluation of coupled processes for CO_2 in aquifers. The nanoparticle research focuses on the mobile fractions and natural abundance in soils. Also studied is the rate of infiltration in the unsaturated zone, an important issue in studying and defining the driving forces and boundary conditions in the containment and cleanup of contaminants in the subsurface. Also being researched are interfacial reactions such as at quartz/water interfaces and the intergranular diffusion in uranium and in sand. Another study has focused on the use of x-ray absorption and diffraction methods to study sorption processes.

ISOTOPE GEOCHEMISTRY

The Center for Isotope Geochemistry (CIG) is a state-of-the-art analytical facility established in 1988 to measure the concentrations and isotopic compositions of elements in rocks, minerals, and fluids in the earth's crust, atmosphere, and oceans. Fundamental research conducted at this center is directed at finding new ways to use isotopic information to study earth processes, such as long-term climate changes, and at predicting the chemical transport of mantle-derived or deep crustal fluids as they move through the crust.

One of the major problems being studied at CIG is how to estimate fluid-solid reaction rates in natural-groundwater higher-temperature geothermal conditions, particularly as these rates affect mineral dissolution and secondary mineral precipitation. ESD researchers are developing novel ways of estimating reaction rates by using isotopic tracers (primarily strontium, but also uranium and neodymium) to determine solid-fluid exchange rates in various natural situations. Scientists are able to derive the "reaction length," a parameter that depends on the ratio of isotope transport by diffusion and advection to the reaction rate. The ultimate objective is to understand the microscopic (as well as pore-scale and mesoscale) characteristics of natural systems that have been characterized in terms of "field scale" reaction-rate measures. An intermediate goal is to establish empirically the natural range of fluid-solid reaction rates. Examples are the U-Th/He geochronology of young volcanic rock, understanding and predicting the microbial degradation of chlorinated solvents with carbon isotopes, and using Xenon isotopes to study buried wastes.

ADVANCED COMPUTATION FOR EARTH IMAGING

The Center for Computational Seismology (CCS) was created in 1983 as the Berkeley Lab and UC Berkeley nucleus for seismic research related to data processing, advanced imaging, and visualization. In recent years, a great deal of cross-fertilization between seismologists and other geophysicists and hydrogeologists has developed within the division, resulting in collaborations on a wide variety of fundamental imaging problems. A primary thrust in this research has been to jointly develop seismic and electrical methods for understanding fluid flow and properties within the subsurface. In addition, fundamental studies on improved inversion and modeling of complex media in 3-D are being carried out to analyze such effects as matrix heterogeneity fluid flow and anisotropy. Applications range from small-scale environmental problems to oil and gas reservoirs.

ROCK PHYSICS

A variety of rock and soil science experiments are being conducted through ESD's Geoscience Measurements Facility, which supports both field and laboratory work. In one new laboratory project, researchers are studying the compaction and fracturing of weakly cemented granular rocks. This study examines the effect of micromechanical properties of weak granular rock on macroscopic properties such as load-displacement response, ultimate strength, and failure mode. In a second study, a fundamental investigation of scattering and intrinsic attenuation of seismic waves in rock with heterogeneous distributions of fluids and gas is being conducted. This research represents a departure from past rock-physics studies on seismic attenuation, in that the emphasis here is not to do a detailed study of a specific attenuation mechanism, but rather to investigate theoretical and laboratory methods for obtaining separate estimates of scattering and intrinsic attenuation in rock with heterogeneous pore-fluid distributions.

FUNDING

http://www-esd.lbl.gov/

U-Th/He Geochronology of Young Volcanic Rocks

Sarah Aciego, Donald J. DePaolo, and B. Mack Kennedy
Contact: Sarah Aciego, 510/486-4975, aciego@uclink.berkeley.edu

RESEARCH OBJECTIVES

Constraining time scales for Quaternary (<1.8 my) events remains a challenge. Despite considerable progress in C-14 and Ar-Ar dating, no single method with wide applicability has emerged. This project investigates the use of the U-Th/He system for dating young volcanic rocks, which is based on the accumulation and retention of ^{4}He from decay of U and Th in mineral grains.

APPROACH

The first step was to assess technique viability by analyzing young samples of known age: garnets from the 79 AD eruption of Mt Vesuvius. The second was application to a system that could benefit from direct age measurements, but for which only cursory knowledge of age is known: olivine phenocrysts from a suite of Hawaiian basalts.

Inherent in the application of the U-Th/He technique are several sources of error that must be addressed. First, typical minerals (garnet, olivine) have low and heterogeneous U,Th concentrations, making measurement of U,Th, and He concentrations difficult and necessitating measurement on the same aliquot. A furnace was designed capable of melting 1–2 g samples in platinum containers from which the melted sample can be retrieved for U,Th determination. Second, basalt matrix often has more U and Th than the embedded phenocrysts, leading to additional helium accumulation in the phenocryts by alpha recoil implantation. Modeling indicates that for a given matrix/phenocrysts (U,Th) concentration ratio, the magnitude of the age correction is strongly dependent on grain size (Figure 1). Furthermore, the correction assumes perfect extraction of unbroken phenocrysts from the matrix. The range of recoiled alpha particles is on the order of 10's of microns. Therefore, to overcome alpha recoil effects, we abrade samples, removing the exterior portions that are most effected. Since the matrix/phenocryst U,Th concentration ratio in the Vesuvian garnets is close to one, the correction is negligible. However, the high ratio in Hawaiian lavas is more problematic. To assess our abrasion technique, we analyzed abraded and nonabraded olivine aliquots to compare alpha recoil model ages with those determined directly from the abraded samples.

ACCOMPLISHMENTS

We successfully determined the age of the 79 AD eruption of Mt Vesuvius within analytical error. Analyses of abraded and nonabraded samples indicated that the alpha recoil model overcorrects for injection of radiogenic helium. Detailed analysis of the accuracy of abrasion is still required, but this initial investigation indicates that it is possible to date young olivine samples with low U,Th concentrations, despite high concentrations in the matrix. For two Hawaiian samples, the calculated ages of 329 kyr and 189 kyr fall within the age range constrained by previous methods.

SIGNIFICANCE OF FINDINGS

We have demonstrated the ability to date Quaternary volcanic samples, indicating that the U-Th/He method can be used as a reliable geochronological tool. Extension of the technique will vastly improve constraints on time scales for Quaternary events.
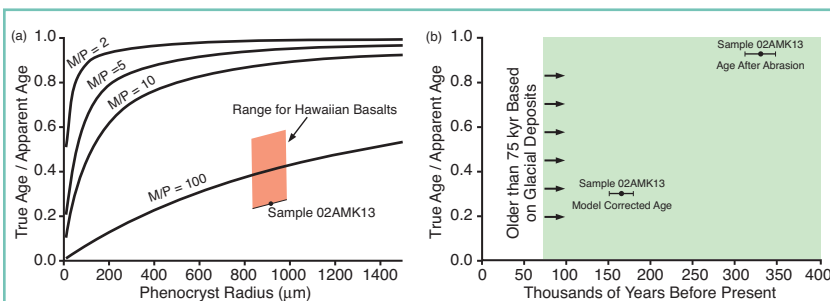

Figure 1. (a) Contours of age correction factors as a function of grain size, using varying matrix/phenocryst (M/P) concentrations of U and Th. Also plotted are the range of correction factors for Hawaiian samples using measured [U,Th] and U-series isotopes. Sample 02AMK13 has a M/P ratio of 145 and a 800–1,000 µm grain size, which corresponds to a correction factor of 0.32. (b) Comparison of ages for sample 02AMK13 constrained by glacial deposits—shown are calculated ages plotted against the correction for alpha recoil; the unabraided sample has a model correction factor of 0.32, while the abraded sample requires no alpha recoil correction and thus has a correction factor of 1.

RELATED PUBLICATION

Aciego, S.M., B.M. Kennedy, D.J. DePaolo, J.N. Christensen, and I. Hutcheon, U-Th/He age of phenocrystic garnet from the 79 AD eruption of Mt. Vesuvius. Earth and Planetary Science Letters, 216, 209–219, 2003. Berkeley Lab Report LBNL-53622.

ACKNOWLEDGMENTS

Monitoring Microbial Degradation of Chlorinated Solvents with Carbon Isotopes

Mark Conrad, Patrick Lee[1], Shaily Mahendra[1], Kung-Hui Chu[2], and Lisa Alvarez-Cohen
[1] University of California, Berkeley, [2] University of Tennessee, Knoxville
Contact: Mark Conrad, 510/486-6141, msconrad@lbl.gov

RESEARCH OBJECTIVES

Chlorinated solvents are common groundwater contaminants. Because of their high density (greater than water) and low solubility, they are extremely difficult to remove from groundwater using standard remedial techniques such as pump-and-treat. *In situ* bacterial degradation of these compounds represents one alternative solution to this problem. However, it is very difficult to verify that these processes are actually occurring. One promising technique for monitoring subsurface microbial activity is to measure the carbon isotopic compositions of the contaminants and their degradation byproducts. Because microbial degradation of organic compounds favors breaking bonds with ^{12}C rather than ^{13}C, the isotopic ratio of the substrates tends to become enriched in ^{13}C. As a result, with a good understanding of the magnitude of the shift in the carbon isotope ratios caused by a specific process, we can determine the degree of degradation that has occurred. The purpose of this research is to quantify the carbon isotopic fractionation caused by different biologic processes known to degrade chlorinated solvents.

APPROACH

We have concentrated our studies on bioremediation of chlorinated ethenes that include some of the most toxic and recalcitrant chlorinated solvents, including perchloroethylene (PCE), trichloroethylene (TCE), isomers of dichloroethylene (DCE), and vinyl chloride (VC). These compounds can be anaerobically degraded by reductive dechlorination (whereby chloride ions are stripped from the molecules, progressively converting the contaminants from PCE to TCE to DCE to VC to ethene). Some organisms are only capable of completing one of these steps, whereas others can do more than one. Under aerobic conditions, chlorinated ethenes can also be oxidized to nontoxic end products (chloride ions and carbon dioxide) by several different oxygenase-expressing cultures. Some of the oxygenase-catalyzed degradations are metabolic (yielding energy and carbon for cell growth), while others are co-metabolic (providing no energy to the cells). Most prior studies of carbon isotope fractionation during biodegradation of chlorinated ethenes have used mixed cultures enriched from field sites where degradation is suspected. However, the results of these studies are variable. We are performing a series of experiments with pure cultures to determine how organisms using different mechanisms fractionate carbon isotopes.

ACCOMPLISHMENTS

We have completed and published a study of carbon isotope fractionation during aerobic degradation of chlorinated ethenes. The observed shifts were small (<1‰) for degradation of all of our experiments except those with VC, which were as high as 6‰. A series of anaerobic experiments with pure cultures are currently in progress. The carbon isotopic fractionation effects we have observed for these experiments are much larger (15 to 33‰, depending on the organism and the substrate) than for aerobic processes.

SIGNIFICANCE OF FINDINGS

The results of our work demonstrate that there can be significant differences in the magnitude of carbon isotope fractionation during biodegradation of chlorinated ethylenes, depending on the organisms involved and the metabolic process utilized. These differences can be used to determine which organisms are present and active in the field. When coupled with microbial genetic studies, this will lead to a comprehensive understanding of intrinsic bioremediation processes occurring at field sites. This understanding can be used to guide efforts to enhance biodegradation of the chlorinated solvents, by adding nutrients or bacteria to the system, and to monitor the success of these efforts.

RELATED PUBLICATIONS

Chu, K.-H., S. Mahendra, D.L. Song, M.E. Conrad, and L. Alvarez-Cohen, Stable carbon isotope fractionation during aerobic biodegradation of chlorinated ethenes. Environ. Sci. Technol., 38, 3126–3130, 2004. Berkeley Lab Report LBNL-55658.

Song, D.L., M.E. Conrad, K.S. Sorenson and L. Alvarez-Cohen, Stable carbon isotope fractionation during enhanced in-situ bioremediation of trichloroethene. Environ. Sci. Technol. 36, 2262–2268, 2002. Berkeley Lab Report LBNL-50047.

ACKNOWLEDGMENTS

URANIUM ISOTOPE COMMINUTION AGES:
A NEW WAY TO STUDY SEDIMENTATION PROCESSES

Donald J. DePaolo, Katherine Maher, and John N. Christensen

Contact: Don DePaolo, 510/643-5064, depaolo@eps.berkeley.edu

RESEARCH OBJECTIVES

Erosion is a fundamental Earth process, in which rocks are broken down by mechanical and chemical means into small fragments and transported by streams, glaciers, winds, and ocean currents, ultimately to accumulate as sediment on the ocean floor, or in lakes, or river floodplains. The time that it takes for individual particles to travel from the their source to the site of deposition can be roughly estimated using material balance calculations, but there has not been a means to measure it. In the course of research using uranium (U) isotopes to measure weathering rates of soils and sediments, we have discovered a means to measure the transport times of sedimentary particles. This method now allows us to evaluate how transport time changes with climate, tectonic activity, and other factors, and may also be useful for dating nonmarine sediments and atmospheric dust.
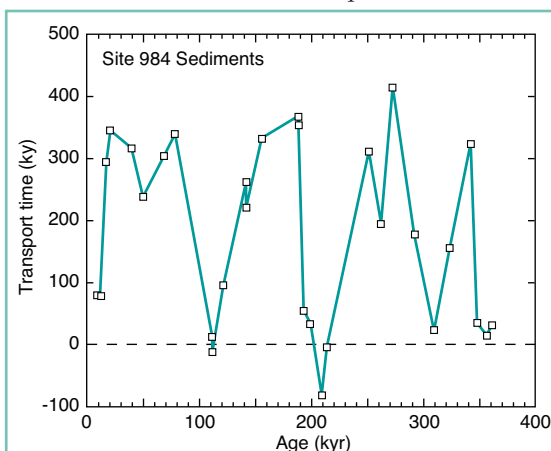

Figure 1. Calculated transport time (from sediment source to site of deposition) for fine-grained silicate fraction of sediment from ODP Site 984 in the North Atlantic. During interglacial periods, transport is rapid; during glacial times, it is much slower. The relationship between glaciation and transport time is less simple for age greater than 250 thousand years. Measured $^{234}U/^{238}U$ activity ratios vary from 0.83 to 0.97.

APPROACH

The basis for the method is that the $^{234}U/^{238}U$ ratio of sedimentary particulates of diameter less than about 50 μm measures the age of the particle. The "clock" is provided by the disruption of the normal ^{238}U decay series resulting from the loss of the ^{238}U decay product, ^{234}Th, by recoil during alpha decay of ^{238}U. When a small mineral grain is produced by erosion, it begins to leak ^{234}Th to its surroundings, and its $^{234}U/^{238}U$ ratio starts to decrease. To reach the steady-state $^{234}U/^{238}U$ ratio appropriate to its size requires about 1 million years, during which time the $^{234}U/^{238}U$ is measuring the time since the small grain was produced, which we refer to as the "comminution age." If the time between production of the small grains and deposition on the sea floor is relatively short (10,000 years or less), then the particles will still have $^{234}U/^{238}U$ activity ratios that are close to 1.0. If the time scale for transport to the ultimate site of deposition is much longer (≥100,000 years), then the grains will be deposited with a $^{234}U/^{238}U$ activity ratio significantly less than 1.0. Typical depletions in ^{234}U in fine-grained sediments are 5% to 30%, and this depletion can be measured to ±0.1% using multicollector inductively coupled plasma mass spectroscopy (ICPMS).

ACCOMPLISHMENTS

Data have been collected for a clastic deep sea sedimentary sequence from Ocean Drilling Program (ODP) Site 984A in the North Atlantic. The sediments contain primary marine carbonate and authigenic components, and hence were first leached with hydrochloric acid. The data show cyclic variations in the measured $^{234}U/^{238}U$ activity ratio, indicating that transport time for sediment to this site has varied considerably with time (Figure 1). Comparison with O isotope records and Nd and Sr isotopes shows that the transport time variations correlate with glacial cycles, and that the source of the sediment also shifts as the transport time changes. During interglacials, the sediment is dominated by material derived from Iceland and transported rapidly to the site of deposition. During glacials, the sediment is from a continental source and has a long transport time, probably because Iceland is surrounded by sea ice and the deposition is either aeolian or redistributed from exposed continental shelves.

SIGNIFICANCE OF FINDINGS

The U isotope comminution age model may open up new ways of understanding the movement of sediment and dust on the Earth. The method may be useful for dating glacial moraine, loess, lake and river sediments, and for determining the sources of atmospheric mineral dust.

RELATED PUBLICATION

Maher, K., D.J. DePaolo, and J.C. Lin, Rates of diagenetic reactions in deep-sea sediment: In-situ measurement using $^{234}U/^{238}U$ of pore fluids. Geochimica et Cosmochimica Acta, 68 (22), 4629–4648, 2004. Berkeley Lab Report LBNL-56681.

ACKNOWLEDGMENTS

FLOWING-FLUID ELECTRIC-CONDUCTIVITY LOGGING FOR HYDROLOGIC CHARACTERIZATION OF FRACTURED ROCK

Christine Doughty and Chin-Fu Tsang
Contact: Christine Doughty, 510/486-6453, cadoughty@lbl.gov

RESEARCH OBJECTIVES

For the study of flow and transport in the subsurface, knowledge of flow zones and their hydraulic properties is essential. Boreholes drilled deep into the rock are often employed to determine this information. Coring and geophysical methods may be able to identify the fractures themselves, but they are unlikely to provide information on fracture flow properties. Straddle-packer pump testing yields fracture flow properties, but is very time-consuming and expensive. Flow-logging techniques are an attractive alternative—they are sensitive to fracture flow and are efficient to deploy in the field. The objective of the present work is to develop the theory for the multi-rate flowing fluid-electric-conductivity (FEC) logging method and demonstrate its application to field data.

APPROACH

The flowing FEC logging method involves the replacement of wellbore water by de-ionized or constant-salinity water, followed by constant pumping with rate Q, during which a series of FEC logs are taken. The logs can be analyzed to identify depth locations of inflow, as well as evaluate the transmissivity and electric conductivity (salinity) of the fluid at each inflow point. When the method is repeated with two or more pumping rates, a combined analysis of the multi-rate data allows an efficient means of determining transmissivity and salinity values of all inflow points—as well as their inherent (so-called far-field) pressure heads.

ACCOMPLISHMENTS

Flowing FEC logging was performed in Well DH-2, very close to the Japan Nuclear Cycle Development Institute's MIU (Mizunami Underground Research Laboratory) site in the Tono area of Gifu Prefecture, Japan. Well DH-2 is about 500 m deep; the upper 167 m penetrates tertiary sedimentary rocks, which unconformably overlie a medium-grained biotite granite of Cretaceous age that is weathered and highly fractured. Flowing FEC logging was repeated three times, using pumping rates of 10 L/min, 20 L/min, and 5 L/min. The suite of FEC logs for each pumping rate were matched (through trial and error) by varying feed-point strength and salinity. Feed-point salinity is constrained to remain the same for each pumping rate, whereas the variation in feed-point strength with pumping rate provides the basis for determining feed-point transmissivity and inherent pressure head.
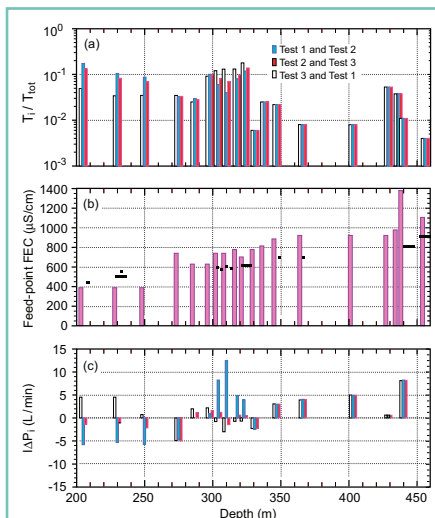

Figure 1. Results of multi-rate flowing FEC logging: (a) feed-point transmissivity normalized by total transmissivity of the borehole; (b) feed-point salinity (the black segments show independent salinity information, which was not used in the present analysis); (c) normalized inherent pressure head of feed-points (IDPi = 0 corresponds to the pressure head of the wellbore as a whole under zero pumping conditions).

Performing the flowing FEC logging method at different pumping rates has enabled us not only to estimate inflow strengths and salinities of hydraulically conductive fractures intersecting Well DH-2, but also to compare their transmissivities and inherent pressure heads (Figure 1). Moreover, using three pumping rates provides a consistency check on the analysis, supplying a measure of the uncertainty within the results. Comparisons against static FEC profiles and independent chemical, geological, and hydrogeological data provide further checks on the validity of the multi-rate flowing FEC logging-method results.

SIGNIFICANCE OF FINDINGS

Flowing FEC logging provides an efficient, affordable means of characterizing the hydraulically conductive features intersecting a borehole with high vertical resolution. Such information is invaluable for characterization of regional groundwater flow, design of nuclear waste storage facilities, remediation of subsurface contamination, and a host of other issues. Moreover, it can be very useful in conjunction with other subsurface site characterization activities, such as providing high-resolution monitoring during a tracer test, or providing ground truth at boreholes for crosshole geophysical imaging methods.

RELATED PUBLICATIONS

Tsang, C.-F., and C. Doughty, Multi-rate flowing fluid electric conductivity logging method. Water Resour. Res., 39(12), 1354 (10.1029/2003WR002308), 2003. Berkeley Lab Report LBNL-52518

Doughty, C., S. Takeuchi, K. Amano, M. Shimo, and C.-F. Tsang, Application of multi-rate flowing fluid electric conductivity logging method to Well DH-2, Tono Site, Japan. Water Resour. Res. (in press), 2005. Berkeley Lab Report LBNL-56479.

ACKNOWLEDGMENTS

XENON ISOTOPES RELEASED FROM BURIED TRANSURANIC WASTES

Evan Dresel and B. Mack Kennedy
Contact: Mack Kennedy, 510/486-6451, bmkennedy@lbl.gov

RESEARCH OBJECTIVES

This project addresses the Department of Energy need to characterize and assess the location, type, and mobility of wastes in the subsurface. The specific objective is to evaluate the use of xenon isotopes in soil gases to detect the presence of radioactive transuranic wastes, characterize the waste, and model the transport of fission xenon through the unsaturated soil gas environment.
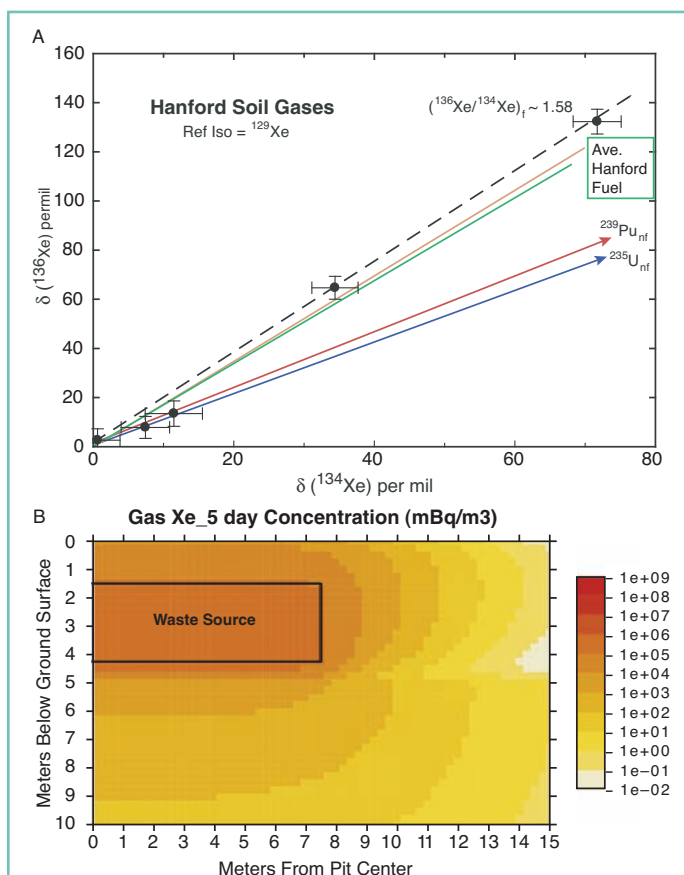

Figure 1. A: Isotopic composition of xenon in Hanford soil gases. Dashed line is a least squares fit to the data. Solid lines represent the composition of various fission sources, including the composition expected for Hanford fuel rods (orange and green lines). B: Modeled distribution of ^{133}Xe in the vadose zone relative to a waste source and constrained by the the values measured in the soil gases.

APPROACH

Xenon is a chemically inert noble gas and therefore a conservative tracer under most geologic conditions. Several stable and short-lived radioactive xenon isotopes are produced as fission products in nuclear reactors and through spontaneous fission. The isotopic composition of fission-produced xenon will have a characteristic yield pattern that can be used (1) to detect fission xenon in soil gases saturated with ambient atmospheric

xenon, and (2) as a diagnostic tool for characterizing the fission source(s). Presence of short-lived fission xenon isotopes (^{133}Xe, $t_{1/2}$ = 5.24 days; ^{135}Xe, $t_{1/2}$ = 9 hours) in surrounding soil gases would confirm ongoing fission in the buried waste—and (under optimal conditions) could be used to set limits on leakage rates from the buried waste containers, as well as transport and residence times in the soil gas environment.

ACCOMPLISHMENTS

Initial measurements of soil gases collected near disposal facilities at the U.S. Department of Energy's Hanford site clearly show both stable and radio-xenon isotopic signatures indicative of transuranic waste. The isotopic composition of the stable fission-xenon isotopes closely matches that calculated for production from Hanford's unenriched and enriched Zr-clad fuel (Figure 1A). Radio-xenon isotopes were also detected, and their abundances have been used in a multiphase vadose zone transport model that indicates transport from the waste source is at a sufficient rate to be detected up to 10's of meters away. Additional data will be needed to constrain leakage rates from the waste container.

SIGNIFICANCE OF FINDINGS

Remediation of buried transuranic and other waste is one of the most difficult and costly environmental issues at U.S. Department of Energy sites. This project addresses the DOE need to characterize and assess the location and mobility of wastes in the subsurface. We have demonstrated that xenon isotopes released to the vadose zone from transuranic wastes provide unique tracers for source identification and the study of vadose zone transport processes, as well as having potential for constraining leakage rates from buried containers.

RELATED PUBLICATIONS

Dresel, P.E., and S.R. Waichler, Evaluation of xenon gas detection as a means for identifying buried transuranic waste at the Radioactive Waste Management Complex, Idaho National Environmental and Engineering Laboratory. PNNL-14617, Pacific Northwest National Laboratory, Richland, Washington, 2004.

Dresel, P.E., S.R. Waichler, B.M. Kennedy, J.C. Hayes, J.I. McIntyre, J.R. Giles, and A.J. Sondrup, Xenon isotope releases from buried transuranic waste. Trans. Am. Geophys. Un., Fall Meeting, San Francisco, CA, 2005.

ACKNOWLEDGMENTS

http://www-esd.lbl.gov/

REGIONAL TRENDS IN HELIUM ISOTOPES:
EVIDENCE FOR DEEP PERMEABILITY IN THE BASIN AND RANGE

B. Mack Kennedy and M. C. van Soest
Contact: B. Mack Kennedy, 510/486-6451, bmkennedy@lbl.gov

RESEARCH OBJECTIVES

The Basin and Range Province of western North America is characterized by an anomalous geothermal gradient that has created a vast region of exceptional potential for geothermal energy development. However, first-order exploration techniques are difficult to apply: by the time deep fluids emerge at the surface, they have re-equilibrated at lower temperatures, overprinting chemical and isotopic compositions that might otherwise provide evidence for deeper high-temperature reservoirs. In essence, the geothermal systems are "hidden." This project maps regional trends in helium isotopic compositions that may detect local zones of deep permeability where surface waters, penetrating deep in the crust, can be heated to form potential geothermal systems.
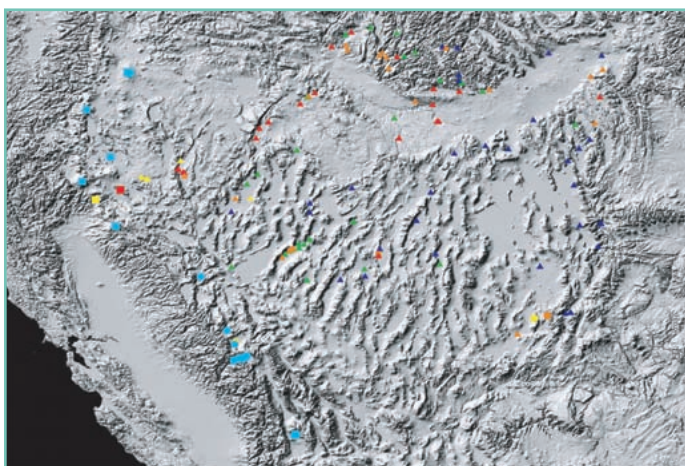

Figure 1. Shaded relief map of the Basin and Range (BR) and nearby surrounding areas. Locations are shown for hot spring and hot well samples for the BR, the Snake River Plain (SRP), the Idaho Batholith (IBL), and for some of the Cascade volcanoes (CV). Some geographical locations are identified. Data from this study, Welhan et al. 1988, and Jenkins, unpublished data (used with permission).

Symbols are shape and color coded to indicate magnitude of $^3He/^4He$ ratio and heat source:
1. Filled circles: BR magmatic heat source or possible BR magmatic heat source.
2. Filled triangles: BR extensional heat source. The samples from the SRP and IBL are included in this catagory until a better assessment of their heat source can be made.
3. Filled squares: CV magmatic heat source.
4. Filled diamonds: BR/CV transitional - unclear heat source: a geothermal well and two springs near Canby, CA.
Color coding is as follows:
Blue ≤ 0.3 Ra; 0.3 > Green ≤ 0.6 Ra; 0.6 > Orange ≤ 1.0 Ra; 1.0 > Red ≤ 2.0 Ra; 2.0 > Yellow ≤ 3.0 Ra; Cyan > 3.0 Ra.

APPROACH

The focus of the project is the relationship between known Basin and Range geothermal resources and the presence of fault-hosted, deep, permeable fluid-flow pathways, as identified by anomalous helium isotopic compositions in surface fluids. The anomalies are defined as high helium-isotopic ratios relative to a regional trend. Helium isotopes are of particular interest because they provide unequivocal evidence for the presence in crustal fluids of mantle-derived volatiles that can only be acquired by deep fluid circulation.

ACCOMPLISHMENTS

We have found that exceptionally high helium-isotopic compositions (~3-6 Ra—Ra is the ratio in air) are confined to the western margin of the Basin and Range (Figure 1) coinciding with a zone of active volcanism, extending along the eastern Sierra into the Cascade volcanic complex of northern California and Oregon. Moving east, there is a general decline to values as low as ~0.1 Ra. Superimposed on this trend are localized zones of high helium-isotopic compositions (e.g., DV, DIV, BRD). A detailed study of one of these "He-spikes" (DV, Dixie Valley) found that high ratios were restricted to fluids emerging directly from an active high-angle normal fault that hosts one of the most successful geothermal fields in Nevada. The high ratios require deep permeability consistent with the presence of high-temperature exploitable fluids rising through the fault. The other "He-spikes" occurring throughout the Basin and Range may also indicate deep permeability and high potential for geothermal development.

SIGNIFICANCE OF FINDINGS

Deep permeable pathways are a necessity in the development of viable nonvolcanic geothermal resources in the Basin and Range. The deep pathways provide access to high temperature and can host fluid convection cells. Helium isotopes may provide the best and perhaps only tool for detecting faults with deep and high-enough permeability to develop economic geothermal systems.

RELATED PUBLICATIONS

Kennedy, B.M. and M.C. van Soest, A helium isotope perspective on the Dixie Valley, Nevada hydrothermal system. Geothermics (submitted), 2005.

Kennedy, B.M. and M.C. van Soest, Regional and local trends in helium isotopes, Basin and Range Province, Western North America: Evidence for deep permeable pathways. Geothermal Resources Council, Trans (submitted), 2005.

ACKNOWLEDGMENTS

BERKELEY LAB
http://www-esd.lbl.gov/

STUDIES OF THE FORMATION, STRUCTURE, AND REACTIVITY OF NANOPARTICULATE GOETHITE

Christopher Kim, Glenn Waychunas, and Jillian Banfield[1]

[1]UC Berkeley, Dept. of Earth and Planetary Sciences

Contact: Glenn Waychunas, 510/495-2224. GAWaychunas@lbl.gov

RESEARCH OBJECTIVES

Goethite is a ubiquitous mineral in soils and sediments, and recent work (Van Der Zee et al., 2003) suggests that on the nanoscale it is also the dominant Fe oxyhydroxide in lacustrine and marine sediments. Goethite nanoparticles may have markedly different properties than their larger analogs, including sorption capabilities, surface charges, aggregation, and redox capability (Waychunas et al., 2005). In analogy to our work with nanosize sphalerite (Gilbert et al., 2004), there may also be important phase transformations in both molecular and magnetic structure as a function of size. We thus wish to prepare monodispersed nanogoethite from a few nanometers to 100 nm in diameter, and determine the changes in structure and chemical reactivity over this range.
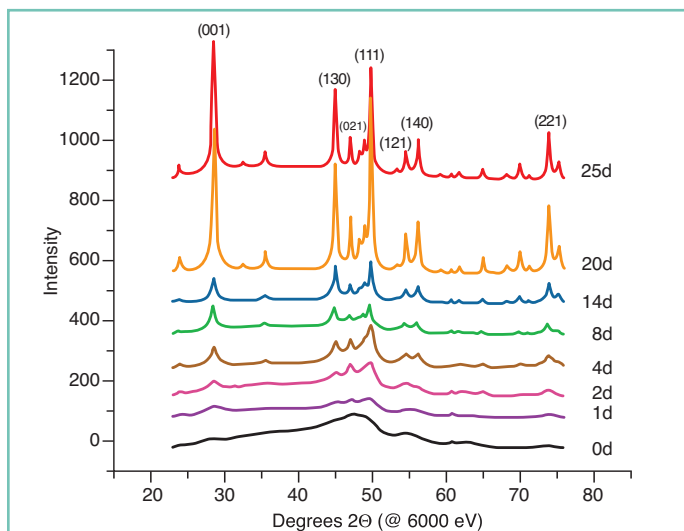

Figure 1. Synchrotron x-ray diffraction patterns of nanogoethite grown for varying periods at 90° C obtained on ALS beamline 7.3.3. Goethite Bragg peaks are labeled with Miller indices. Particle size ranges from 4 nm (0 days) to ~100 nm (25 days).

APPROACH

Nanogoethites were prepared by rapid microwave heating of a ferric nitrate solution, followed by rapid cooling. The resultant solution was aged for up to 33 days at 90°C, with aliquots taken during this period having progressively larger crystallites. Size distributions were obtained via dynamic light scattering (DLS), small angle x-ray scattering (SAXS), and via transmission electron microscopy (TEM) measurements. The crystallization process was also studied in real time by SAXS studies at the Advanced Photon Source (APS). Crystallites were monodispersed and from 4 to 120 nm in diameter, with shape variations during growth. The smallest crystallites were equiaxial, but assembled into rodlike forms in the 30 nm size range. Wide-angle x-ray scattering patterns were obtained for all goethites, including a series over the full coarsening period (Figure 1), and a more detailed analysis of the smallest crystallites at the APS. Sorption of a series of metals (Hg, Zn, As [as arsenate], and Cu) was done over the whole size range, and the samples studied via extended x-ray absorption fine structure (EXAFS) analysis at SSRL.

ACCOMPLISHMENTS

All the sorption studies indicated a change in the character of the metal sorption complexes in the smallest nanogoethites, suggesting differences in the nature of the surface attachment sites. X-ray scattering studies were also consistent, with the smallest crystallites deviating in structure from bulk goethite. Ongoing work involves examining how the nanogoethites change with aging at low temperatures, and the precise nature of aggregation. TEM analysis suggests oriented aggregation processes occur at the smaller size regimes (4–10 nm), leading to nonclassical growth, while larger (30+ nm) nanogoethite grows by classical monomer addition.

SIGNIFICANCE OF FINDINGS

The results verify that nanogoethite reacts differently from larger sized crystallites and has different molecular surface structure. This suggests that studies done with coarser samples may overlook processes that would occur in sediments where goethite is forming. There also may be changes in sorbed species as nanogoethite ages, particularly when oriented aggregation occurs.

RELATED PUBLICATIONS

Gilbert, B., H. Zhang, F. Huang, J. Banfield, Y. Ren, D. Haskel, J. Lang, G. Srajer, A. Jurgensen, and G. Waychunas, Analysis and simulation of the structure of nanoparticles that undergo a surface-driven structural transformation. J Chem Phys, 120, 11785–11795, 2004.

van der Zee, C., D.R. Roberts, D.G. Rancourt, and C.P. Slomp, Nanogoethite is the dominant reactive oxyhydroxide phase in lake and marine sediments. Geology, 31, 993–996, 2003.

Waychunas, G.A., C.S. Kim, and J.F. Banfield, Nanoparticulate iron oxide minerals in soils and sediments: Unique properties and contaminant scavenging mechanisms. J. Nanoparticulate Research (in press), 2005.

ACKNOWLEDGMENTS

BERKELEY LAB
http://www-esd.lbl.gov/

Tube-Wave Effects in Crosswell Seismic Data

Valeri Korneev

Contact: 510/486-7214, vakorneev@lbl.gov

RESEARCH OBJECTIVES

The main goal of this project is to develop a new technology that will improve the quality and resolution of seismic monitoring in natural underground reservoirs. The main innovative part of this technology is the use of tube waves as primary signal-carriers, which will provide a relatively inexpensive seismic monitoring method for use during management of real-time fluid production.

APPROACH

A tube wave is an interface wave for a cylindrical boundary between two media, typically borehole fluid and surrounding elastic rock. These waves have large amplitudes and can propagate long distances without substantial decay. They are traditionally regarded as a source of high-amplitude noise in borehole seismic data, and consequently much effort goes into their suppression and elimination from seismic recordings.

Recently, analysis of crosswell seismic data from a gas reservoir in Texas revealed two previously undetected seismic wave effects, recorded 2,000 ft above the reservoir. The first effect is that the dominant late phases on the recordings are tube waves, generated in the source well and converted into laterally propagating waves through gas/water saturated layers that then convert back to tube waves in the receiver well. This tube-wave train correlated with a multilayered reservoir zone structure, suggesting that the recorded wave field strongly depended on reservoir parameters. The second effect is that the recorded field is composed of multiple low-velocity tube waves. Modeling results suggest that imperfect cementation is the likely cause of this phenomenon.

ACCOMPLISHMENTS

How to interpret the strong late phases arriving in the 0.8–2.0-second interval during the crosshole seismic experiments is the key issue for this project. The relatively small travel time (0.2 seconds) for the direct P-wave arrivals suggests that the late phases belong to waves with long propagation paths and/or rather small velocities. This energy propagated in a different mode from the direct P-waves. Apparent velocities of the strongest phases around the 1-second arrival time were estimated to be in the 1,300–1,500 m/s range, which corresponds to propagating tube waves. High (90–100–200–220 Hz) and low (30–40–80–90 Hz) bandpass-filtered data indicate virtually the same results, which suggests negligibly low dispersion in the frequency band under consideration. The traces were cross–correlated with the first-arriving wave-train interval, which enabled measurement of the main peak travel times to better than 0.01-second accuracy. Measured travel times represent upward propagating waves of varying velocities. The almost perfect lateral homogeneity of the formation suggests

that the wave propagation of late arrivals follows a three-legged path: The wave propagates downward as a regular tube wave, then converts into a horizontally propagating wave along some seismically conductive layer. After reaching the receiver well, the wave propagates upwards, splitting into a set of at least six waves of different velocities.
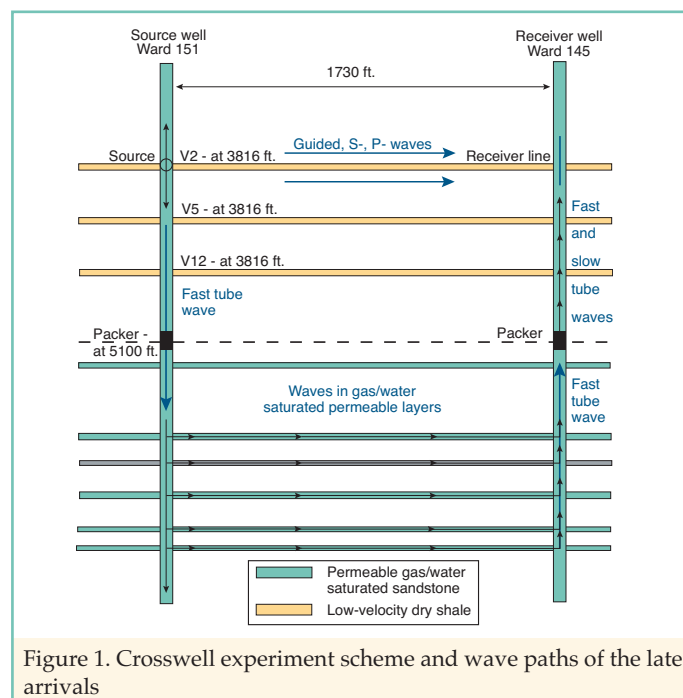

Figure 1. Crosswell experiment scheme and wave paths of the late arrivals

SIGNIFICANCE OF FINDINGS

Because reservoir waves should be affected by reservoir properties (i.e., porosity, permeability, fracture density, and orientation), monitoring based on use of these waves should allow the detection and interpretation of reservoir property changes near production boreholes. These effects can be used to develop a new and promising technology for the imaging and monitoring of underground gas, oil, and water reservoirs.

RELATED PUBLICATION

Korneev, V., J. Parra, and A. Bakulin, Tube-wave effects in crosswell seismic data at Stratton Field. SEG Expanded Abstracts, 2005. Berkeley Lab Report LBNL-53006.

ACKNOWLEDGMENTS

http://www-esd.lbl.gov/

Lattice-Boltzmann Simulation of Isotopic Kinetics in Crystal Growth

Guoping Lu, Donald J. DePaolo, Qinjun Kang[1], and Dongxiao Zhang[1,2]
[1]Los Alamos National Laboratory, [2]University of Oklahoma, Norman, Oklahoma
Contact: Guoping Lu, 510/495-2359, gplu@lbl.gov

RESEARCH OBJECTIVES

Isotope information in waters, sediments, and dust samples can be used to identify their sources. The relevant identification techniques utilize the isotope-ratio variations resulting from fractionation effects caused by the mass difference among the isotopes, with diffusion and reaction among the fundamental processes involved. It is especially important to know isotope behavior associated with these processes, because this determines isotope ratios and the degree of fractionation. This study is aimed at evaluating how fractionations affect the isotopic ratios in phase transformations such as evaporation, condensation, and crystal growth.

APPROACH

We used the Lattice-Boltzmann (LB) method to account for fluid flow, diffusion, and reaction in phase transformations. Isotopic kinetics were investigated by considering both diffusion and reaction rates. The effects of reaction relative to that of diffusion were described with a Damkohler number (Da).

ACCOMPLISHMENTS

LB simulations provide new insights into the behavior of isotopes when evaporation, condensation, or crystal growth occur. Results (Figure 1) show the fractionation effects for a crystal growth under different diffusion-reaction conditions. Kinetic considerations also include degree of oversaturation and the original quantity of mass to be deposited. The isotopic distributions are found to be significantly affected by the diffusive strength of the lighter and heavier isotopes in comparison with the reaction rate.

SIGNIFICANCE OF FINDINGS

LB simulation connects the crystal growth processes and isotopic kinetic effects. The simulation results explain the isotopic variation in evaporation/condensation, snow and ice formation, and crystal growth. Judging from this work, LB simulation shows potential as a method by which to evaluate the fractionation of isotopes in natural systems, extending the present simulation capability to investigate the physics bridging molecular dynamics and the conventional continuum domain.

RELATED PUBLICATIONS

Kang, Q., D. Zhang, P.C. Lichtner, and I. Tsimpanogiannis, Lattice Boltzmann model for crystal growth from supersaturated solution. J. Geophys. Res. Let., 31, L21604, 2004.

Lu, G., D.J. DePaolo, Q. Kang, and D. Zhang. Lattice Boltzmann simulation of isotopic kinetics in phase growths, J. Geophys. Res. Let. (submitted), 2005.
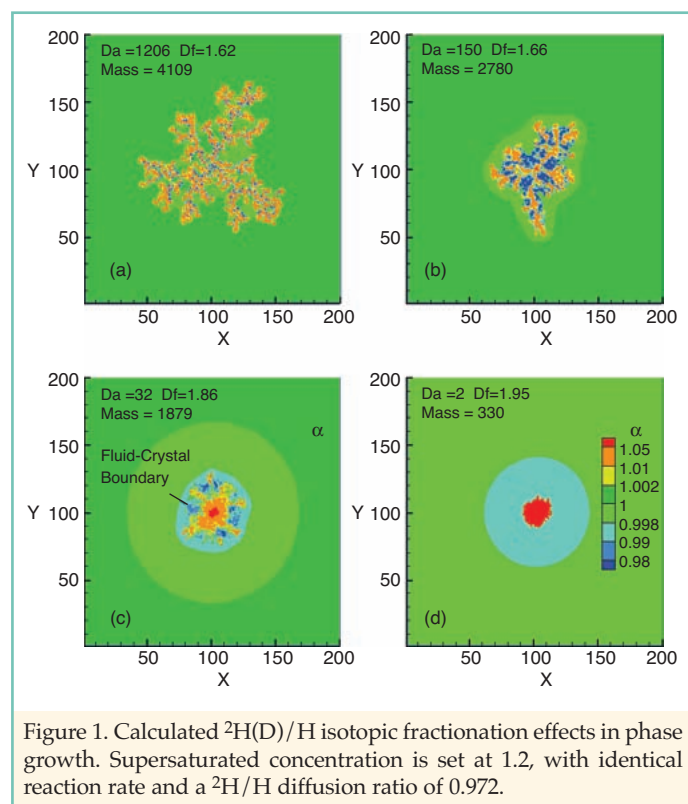
Figure 1. Calculated ^{2}H(D)/H isotopic fractionation effects in phase growth. Supersaturated concentration is set at 1.2, with identical reaction rate and a ^{2}H/H diffusion ratio of 0.972.

ACKNOWLEDGMENTS

THE MINERAL DISSOLUTION RATE CONUNDRUM

Kate Maher, Carl I. Steefel, and Donald J. DePaolo
Contact: Carl Steefel, 510/486-7311, CISteefel@lbl.govct

RESEARCH OBJECTIVES

The objective of this research is to determine whether mechanistic reactive transport modeling of uranium (U) isotopic profiles and major element chemistry (especially alkalinity and calcium) in marine sediments from the North Atlantic Ocean can be used to determine the origin of the apparent discrepancy between laboratory and field mineral dissolution rates.
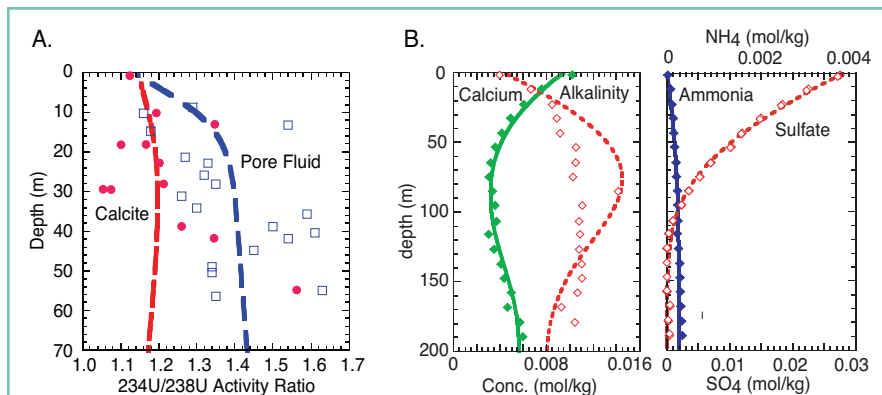

Figure 1A. Uranium isotope activity ratios for calcite (red) and pore fluid (blue). Symbols represent measured values, lines are model results.
Figure 1B. Measured (symbols) and modeled (lines) concentration profiles at Site 984.

APPROACH

Pore-water chemistry and $^{234}U/^{238}U$ activity ratios from fine-grained sediment cored by the Ocean Drilling Project (ODP) at Site 984 in the North Atlantic were used as constraints in modeling *in situ* rates of plagioclase dissolution with the multi-component reactive transport code Crunch. The reactive transport model includes a solid-solution formulation to enable the use of the $^{234}U/^{238}U$ activity ratios in the solid and fluid as a tracer of mineral dissolution.

A suite of reactions, including sulfate reduction and methane production, anaerobic methane oxidation, $CaCO_3$ precipitation, dissolution of plagioclase, and precipitation of secondary clay minerals, along with diffusive transport and fluid and solid burial, control the pore fluid chemistry in Site 984 sediments. The surface area of plagioclase in intimate contact with the pore fluid is estimated to be 3.2 m^2/g, based on both grain geometry and on the depletion of $^{234}U/^{238}U$ in the sediment via α-recoil loss. Various rate laws for plagioclase dissolution are considered in the modeling, including those based on (1) a linear transition state theory (TST) model, (2) a nonlinear dependence on the undersaturation of the pore water with respect to plagioclase, and (3) the effect of Al-inhibition.

RESULTS

The surface area of plagioclase in intimate contact with the pore fluid is estimated to be 3.2 m^2/g, based on both grain geometry and on the depletion of $^{234}U/^{238}U$ in the sediment via α-recoil loss. In the case of the linear TST model, the calculated dissolution rate for plagioclase corresponds to a rate constant that is about 104 to 105 times smaller than the laboratory-measured value. The major element and isotopic methods predict similar dissolution rate constants, if additional lowering of the pore water $^{234}U/^{238}U$ activity ratio is attributed to isotopic exchange via recrystallization of marine calcite, which makes up about 10–20% of the Site 984 sediment. Rate laws based on a nonlinear dependence of the dissolution rate on the solution saturation state, or on inhibition of dissolution by dissolved aluminum, can only account for about one order of magnitude of the apparent discrepancy between laboratory and field rates.

The reactive transport simulations demonstrate that plagioclase dissolution rates depend strongly on the rate of authigenic clay precipitation, since clay precipitation controls both the saturation state of the fluid with respect to plagioclase and dissolved aluminum concentrations. Matching the range of aluminum pore-water concentrations found in deep marine sediments, it appears that slow clay precipitation and/or more soluble clay phases result in close-to-equilibrium conditions with respect to plagioclase, thus effectively removing two to three orders of magnitude from the overall mismatch between laboratory and field rate constants. The remaining two to three orders of magnitude must be attributed to the gradual loss of reactive sites on silicate surfaces with time, which is expected to be more pronounced under close to equilibrium conditions.

SIGNIFICANCE OF FINDINGS

The study indicates that the discrepancy between laboratory and field mineral dissolution rates is real in the case of plagioclase, and that this discrepancy can be attributed to the combination of a control on the saturation state of the plagioclase, exerted by clay precipitation, and the gradual loss of reactivity of the plagioclase surface itself over geologic time.

RELATED PUBLICATIONS

Maher, K., C.I. Steefel, and D. DePaolo, The mineral dissolution rate conundrum: Insights from reactive transport modeling of U isotopes and pore fluid chemistry in marine sediments. Geochimica et Cosmochimica Acta (in press), 2005.

ACKNOWLEDGMENTS

SPLIT HOPKINSON RESONANT BAR EXPERIMENT FOR FRACTURE POROELASTICITY

Seiji Nakagawa, Kurt T. Nihei, and Larry R. Myer

Seiji Nakagawa, 510/486-7894, snakagawa@lbl.gov

RESEARCH OBJECTIVES

The objective of this research is to examine the dynamic poroelastic behavior of single fractures and faults in rock for a range of hydraulic properties. To this day, laboratory experiments on the dynamic properties of single fractures have been conducted nearly exclusively using ultrasonic waves. When extrapolating the laboratory-measured properties to the field, however, large differences in the seismic wave frequencies used in the laboratory (~1 MHz) and the field (~100 Hz–10 kHz) may result, causing significant discrepancies. To overcome this difficulty, we developed an acoustic resonant bar apparatus that can measure the complex elastic moduli of rocks containing fractures in the sonic range (~1 kHz).

Figure 1. Fracture compliance measurement via split Hopkinson resonant bar tests. A sample assembly containing a short rock core suspended within a metal cage is acoustically resonated within a confining cell (A). Using this setup, normal (compressional) and shear compliances of fractures under dry and water-saturated conditions are measured as a function of applied normal stress (B).

APPROACH

Conventional resonant bar tests have been used since the beginning of laboratory acoustic testing of materials. Typically, a resonant bar test measures a resonance frequency and damping (attenuation) of vibrations in a long, bar-shaped sample and relates them to the complex elastic moduli of the material. Since the frequency, or rather, wavelength, of the resonance is determined by the dimension of the sample, we require a longer sample for measuring the moduli at low frequencies. For testing rocks, this can be a problem, since rock cores longer than several inches (corresponding to frequencies of tens to hundreds of kilohertz) are difficult to obtain.

We have adopted an experimental setup from an acoustic test called the split Hopkinson bar test, which employs a short core or disk-shaped rock sample sandwiched between two long slender metal bars (see Figure 1). While a conventional split Hopkinson bar test measures reflected and transmitted waves across the sample, our setup measures the resonance of the whole system, which allows us to determine the material properties more accurately. Because of the extra length and mass added by the attached metal bars, measured resonance frequencies are reduced, which allows us to measure low-frequency properties of the rock sample. The complex elastic moduli of the rock sample are determined via nonlinear numerical inversion, using a one-dimensional wave propagation model, from measured resonance frequencies and attenuation (measured from the width of the resonance peak). For determining the dynamic properties of a fracture, we conduct two sets of measurements, before and after the fracture is introduced in a rock core. The difference in the apparent elastic moduli of the rock core provides the properties of the fracture.

ACCOMPLISHMENTS

We developed an experimental apparatus for measuring acoustic resonance of short core samples (one to four inches in length) under hydrostatic pressure from high-pressure gas. Concurrently, we developed a complex-elastic moduli inversion technique that allows us to extract the moduli of a sample from measured apparent elastic moduli. An important recent improvement was the consideration of the end-effect, which resulted in an apparent increase in the Young's modulus of a short core sample for materials with a high-Poisson's ratio. A series of experiments was conducted on both synthetic materials with known material properties, and natural geomaterials—including unconsolidated sand, well-consolidated sandstone and carbonates (limestone and chalk), and rock cores containing fractures.

SIGNIFICANCE OF FINDINGS

Experiments for a fractured sandstone core demonstrated that the split Hopkinson resonant bar test is very sensitive to the changes in fracture properties: changes in fracture compliance that result in less than 0.1% of wave transmission coefficient across a fracture can be resolved. This allows us to use the current experimental setup for studying the dynamic poroelasticity of a fracture, with good resolution.

RELATED PUBLICATION

Liu, Z., J.W. Rector, K.T. Nihei, L. Tomutsa, L.R. Myer, and S. Nakagawa, Extensional wave attenuation and velocity in partially-saturated sand in the sonic frequency range. Proceedings of the 38th U.S. Rock Mech. Symp., Washington, DC, pp. 141–145, 2001. Berkeley Lab Report LBNL-50831.

ACKNOWLEDGMENTS

UNPRECEDENTED QUARTZ/WATER INTERFACE STRUCTURE DETERMINED BY PHASE-SENSITIVE SUM FREQUENCY VIBRATIONAL SPECTROSCOPY

Victor Ostroverkhov[1], Glenn Waychunas, and Yuen Ron Shen[1]; [1]University of California, Berkeley, Department of Physics

Contact: Glenn Waychunas, 510/495-2224. GAWaychunas@lbl.gov

RESEARCH OBJECTIVES

Natural chemical processes are initiated at interfaces between aqueous solutions and mineral surfaces. Over the past few years, large advances have been made in the elucidation of mineral surface structure in contact with water (e.g., Eng et al., 2000), and metal sorption topologies (Brown and Sturchio, 2002), but much less is understood about the organization of water on surfaces. Water acts to stabilize particular surface molecular geometries, solvate near-surface ions, and promote chemical reactions via proton and electron transfer—but details of these operations are poorly known on a molecular level. Our work seeks to determine water structure on a range of mineral surfaces as a function of pH, ionic strength, and complexation density (Ostroverkhov et al., 2004). We then intend to use this information to bootstrap molecular-dynamics (MD) simulations of interface phenomena, ultimately allowing modeling of interface reactions.

Figure 1. Right: simulated magnitude spectra of interface water having different dipole orientations for the low-frequency ("ice-like") contribution. The spectra appear identical. Left: Decomposition into real and imaginary parts. The dipole orientation effects are clearly visible.

APPROACH

One of the most powerful tools for investigating interface water structure is sum frequency vibrational spectroscopy (SFVS). SFVS is a two-photon process in which tunable infrared (IR) light is mixed with green light at a mineral surface under solution. As a result of the broken symmetry at the interface, there is a small probability that light at the sum frequency of the two light beams will be generated. Studying this signal allows measurement of the vibrational spectrum only of interface species. SFVS has been used for studying air/liquid, solid/liquid, and other types of interfaces, but as usually employed, the method only detects the spectral amplitude. However, we have developed a method for obtaining SFVS spectra containing both amplitude and phase contributions. This is done by using a reference signal of known phase and allowing it to interfere with the SFVS signal from the interface. By doing this for two different phase reference signals, we can deduce the magnitude and both the real and imaginary parts of the SFVS spectrum. Because the imaginary part yields direct information on the orientation of water dipoles, we can obtain more information on interface water than ever previously measured (Figure 1).

ACCOMPLISHMENTS

By using the Phase-Sensitive (PS)-SFVS technique on quartz (0001) surfaces, we found: (1) that the lower-frequency IR band usually attributed to "ice-like" tetrahedrally bonded water is actually composed of two contributions, and (2) that the "ice-like" water molecules orient themselves quite differently from interface "liquid water" in response to pH changes (Ostroverkhow et al., 2005). In particular, the "ice-like" water protons resist reorienting as pH is changed until a relatively large surface charge is produced, whereas the "water-like" protons shift positions readily at slight pH changes above the point of zero charge.

SIGNIFICANCE OF FINDINGS

Our results yield new information that can be precisely compared to MD simulations of interface water, and we have already obtained good agreement using MD performed with the Center of Advanced Materials for Purification of Water with Systems, a National Science Foundation Science and Technology Center. This work should lead to a new level in molecular modeling of interface reactions.

RELATED PUBLICATIONS

Brown, G.E., and N.C. Sturchio, An overview of synchrotron radiation Applications to low temperature geochemistry and environmental science. Reviews in Mineralogy and Geochemistry, 49, 1–115, 2002.

Eng, P.J., T.P. Trainor, G.E. Brown, G.A. Waychunas, M. Newville, S.R. Sutton, and M.L. Rivers, Structure of the hydrated α-$A_{12}O_3$ (0001) surface. Science, 288, 1029, 2000. Berkeley Lab Report LBNL-46490.

Ostroverkhov, V., G.A. Waychunas, and Y.R. Shen, New information on water interfacial structure revealed by phase sensitive surface spectroscopy. Phys Rev Letters, 94, 046102, 2005.

Ostroverkhov, V., G.A. Waychunas, and Y.R. Shen, Water alignment at (0001) surface of α–quartz studied by sum frequency vibrational spectroscopy. Chem. Phys. Lett. 386: 144–148, 2004.

ACKNOWLEDGMENTS

http://www.esd.lbl.gov/
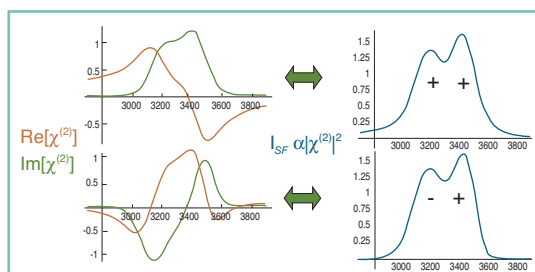
INFILTRATION FLUX DISTRIBUTIONS IN UNSATURATED ROCKS

Tetsu K. Tokunaga, Keith R. Olson, and Jiamin Wan

Contact: Tetsu K. Tokunaga, 510/486-7176, tktokunaga@lbl.gov

RESEARCH OBJECTIVES

The hydrology of unsaturated fractured rocks has received considerable attention over the past two decades. Another category of unsaturated rocks includes talus deposits in mountainous terrain and mine waste rock piles; their hydrology has received little attention. As water percolates through unsaturated rocks, do seepage paths remain uniformly distributed, converge in a manner analogous to river networks, or obey some other principle? This study was aimed at (1) determining whether well-constrained unsaturated flow distributions exist in unconsolidated rock, (2) developing a model consistent with experiments, and (3) identifying similarities between unsaturated flow in unconsolidated rock and in fractured rock.

APPROACHES

Infiltration experiments have been conducted on three different rock types (diabase, sandstone, serpentinite), with rock sizes ranging from 30 mm to 200 mm, and system scales ranging from 1 to 30 rock layers. Water was uniformly applied over the upper surface of the rock packs at various flow rates (all less than 10^{-5} that of the scale-predicted saturated hydraulic conductivity), and spatial distributions of steady state outflow were recorded in arrays of graduated cylinders placed under the lowermost rock layer (Figure 1c). Various flow-path models were developed during the course of this study, allowing individual flow-path trajectories to randomly move downward through successive underlying nearest-neighbor cells.

ACCOMPLISHMENTS

Although individual experiments yielded different spatial distributions of fluxes, we found that probability distributions of fluxes were remarkably similar. Fluxes stabilize into a geometric (exponential) distribution that keeps about half of the system depleted of flow, retains a small fraction of high flow regions, and has a scale equal to the characteristic rock size (Figure 1d). The depth-evolution of the measured flux probability distribution was predicted by modifying a statistical mechanical model, showing that the most probable (maximum entropy) macroscopic distribution of flow paths is equivalent to the Boltzmann distribution.

SIGNIFICANCE OF FINDINGS

These results are important because they have predictive value with respect to probability distributions of fluxes. The geometric distribution of fluxes is expected to be directly applicable to fluxes within talus and waste-rock deposits. Key similarities between infiltration in rock deposits and fractured rock include effectively random downward trajectories (constrained by rock geometry and gravity), balancing of flowpath merging and splitting, and flow occurring at rates many orders of magnitude lower than saturated hydraulic conductivities. These similarities indicate that our results could apply to percolation in fractured rock formations. A better understanding of infiltration path distributions will improve our ability to predict the natural biogeochemical reactive transport rates in unsaturated rocks, as well as help constrain predictions of contaminant migration to underlying groundwaters.
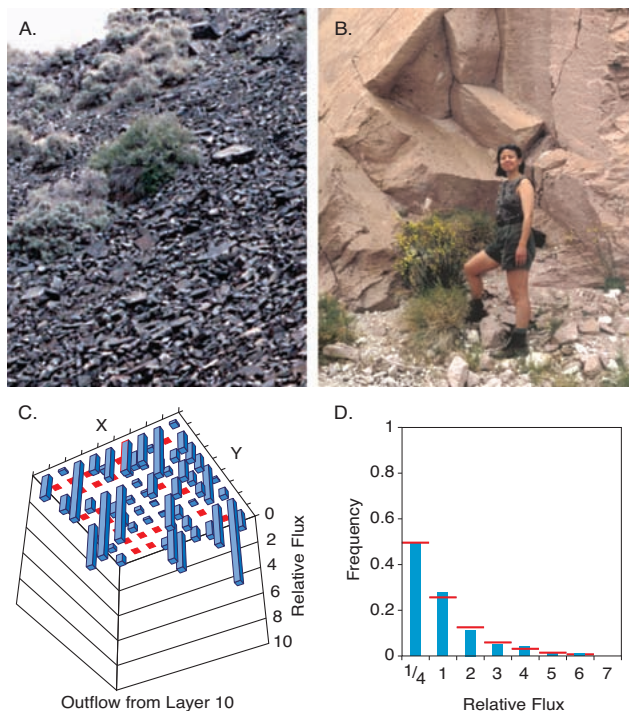

Figure 1A. Talus rock deposit (White Mountains, California); B. Fractured rock (Owens River Gorge, California); C. Spatial distribution of outflow from a rock pack experiment (10 layers); D. Probability distribution of outflow fluxes from a 10-layer rock pack, compared with a geometric distribution model (horizontal red lines).

RELATED PUBLICATION

Tokunaga, T.K., K.R. Olson, and J. Wan, Infiltration flux distributions in unsaturated rock deposits and their potential implications for fractured rock formations. Geophys. Res. Lett. 32, L05404, doi:10.1029/2004GL022203, 2005. Berkeley Lab Report LBNL-57399.

ACKNOWLEDGMENTS

BERKELEY LAB
http://www-esd.lbl.gov/

INTRAGRANULAR DIFFUSION OF URANIUM IN SANDS

Tetsu K. Tokunaga, Jiamin Wan, Stephen R. Sutton[1], and Matt Newville[1];
[1]University of Chicago
Contact: Tetsu K. Tokunaga, 510/486-7176, tktokunaga@lbl.gov

RESEARCH OBJECTIVES

Transport of solutes, including contaminants, in soil and groundwater systems can be complex because of the very wide range of time scales associated with basic processes. Although this complexity can be overlooked in volume-averaged measurements of sufficient size (Figure 1a), more mechanistic understanding of reactive transport requires several progressively finer levels of resolution. One such basic scale in porous media is defined by sizes of individual grains. Intragranular diffusion is often invoked to explain slow mass transfer and reaction rates. Our study uses synchrotron x-ray fluorescence microtomography to directly measure intragranular uranium(VI) diffusion in sediments from Oak Ridge National Laboratory, a DOE facility where uranium (U) contamination has occurred.

APPROACH

Experiments involved exposing 50 to 100 μm sand grains from an uncontaminated area of Oak Ridge to U(VI) solutions, and then obtaining fluorescence microtomographs of intragranular U distributions at different times. The sand grains and U(VI) solutions were contained in sealed micropipette tips and scanned at GSECARS beamline 13ID-C, Advanced Photon Source. In addition to fluorescence microtomography, we applied micro-x-ray absorption near-edge structure (μ-XANES) spectroscopy to determine the oxidation state of U within grains.

ACCOMPLISHMENTS

Fluorescence microtomography maps of U were obtained in real time, over two days of intragranular diffusion. Two-dimensional maps within sands (5 μm resolution) revealed very heterogeneous migration of U into individual grains (Figure 1b). Rates of U uptake inferred from the fluorescence
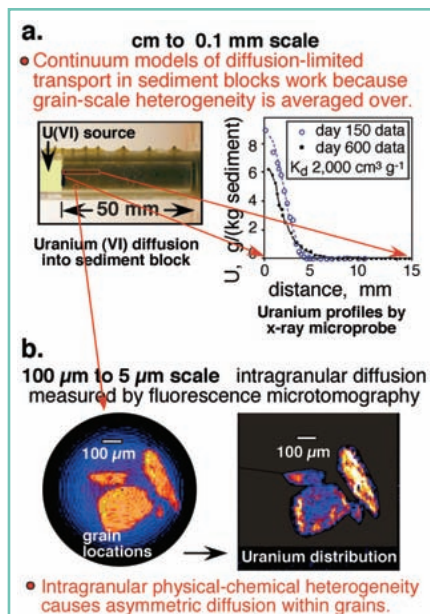

Figure 1. Uranium(VI) diffusion measured at two different scales: (a) at the sediment column scale, diffusion averages over many grains and pores, such that continuum descriptions are directly applicable; (b) at the grain scale, differences associated with mineralogy, secondary coatings, and intragranular properties result in highly heterogeneous U diffusion patterns and control rates for achieving local equilibrium.

maps of grains are consistent with time scales observed in bulk sorption experiments, indicating that intragranular diffusion is in fact the rate-limiting step. Micro-XANES spectra confirmed that U remained as U(VI) during intragranular sorption. Some spatial correlation between U and Fe was also indicated, as expected from the high sorption affinity of U(VI) to Fe(III)-oxide surfaces.

SIGNIFICANCE OF FINDINGS

These results provide proof that intragranular diffusion exerts a major influence on time scales needed for sorption equilibrium of U(VI) in sediments. The fact that most of the sorbed U(VI) in Oak Ridge sediments occurs in intragranular regions has important implications on its reactivity. If most of the U(VI) diffuses into intragranular regions, it does so through typically less than 100 nm pores that would exclude bacteria. Therefore, intragranular redox transformations of U could not occur via direct contact with bacteria, but instead through other redox active solids and solutes, including electron shuttles.

RELATED PUBLICATION

Tokunaga, T.K., J. Wan, J. Pena, S.R. Sutton, and M. Newville, Hexavalent uranium diffusion into soils from concentrated acidic and alkaline solutions. Environ. Sci. Technol., 38, 3056–3062, 2004. Berkeley Lab Report LBNL-54910.

ACKNOWLEDGMENTS

http://www-esd.lbl.gov/

NATURAL ABUNDANCE AND MOBILE FRACTIONS OF NANOPARTICLES IN SOILS

Jiamin Wan, Zuoping Zheng, and Tetsu K. Tokunaga

Contact: Jiamin Wan, 510/486-6004, jmwan@lbl.gov

RESEARCH OBJECTIVES

The current growing interest in nanomaterials and nanotechnology has stimulated the geoscience community to evaluate the roles of nanoparticle phenomena in many of the earth's natural processes. There is currently little quantitative information available on the abundance and mobility of nanoparticles in the subsurface. The importance of natural nanoparticles in facilitating chemical transport can only be evaluated based on knowledge of their inventories and mobility. The objective of this research is to address these two most basic questions: how abundant and how mobile are nanoparticles in the subsurface?
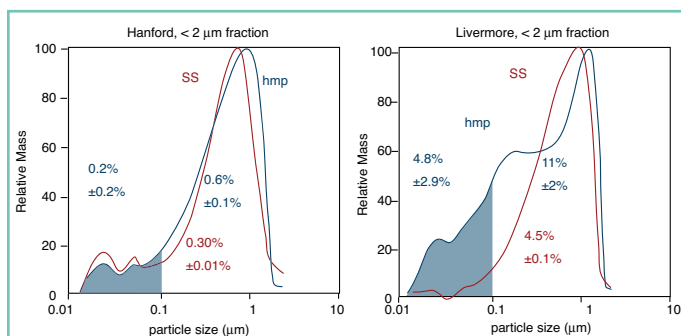

Figure 1. Examples of measured potentially mobile mass (red and ≤ 0.1 μm) vs. mass of total colloid (including nanoparticle) inventory (blue shaded area). For the Hanford soil (pH 8.0), all the dispersible nanoparticle mass is potentially mobile. For the Livermore soil (pH 6.7), only a small fraction of the total dispersible nanoparticle inventory is potentially mobile.

APPROACH

To quantify the influences of soil properties on nanoparticle abundance and mobility, we collected representative types of soils from DOE facilities, including the Oak Ridge, Hanford, Livermore, and Savannah River Sites, all having different mineralogy, soil texture, and pH. Batch equilibrium and column-leaching experiments were conducted using two different kinds of solutions. One was Na-hexametaphosphate, a strong dispersing agent, used to obtain maximum particle releases, thereby defining the total inventories of nanoparticles. The other was a diluted soil pore solution, used to determine potentially mobile

fractions of nanoparticles. In these tests, nanoparticles were defined by an upper effective diameter of 100 nm.

ACCOMPLISHMENTS

We found that: (1) nanoparticles are ubiquitous in soils, and the inventories are proportional to their clay and organic matter fractions; (2) natural nanoparticles in soils consist primarily of common clay minerals and organic matter; and (3) the mobility of nanoparticles is highly pH dependent. No mobile fractions were detected in acidic soils, even when their total nanoparticle inventories were large.

SIGNIFICANCE OF FINDINGS

This research has provided the first survey of mobile nanoparticle inventories of sediments from a variety of subsurface environments. The finding that mobile nanoparticle fractions in natural acidic soils are practically undetectable is an important new insight for the environmental nanogeosciences. These studies will help constrain calculations of subsurface transport associated with nanoparticles.

RELATED PUBLICATIONS

Wan, J., T.K. Tokunaga, E. Saiz, J.T. Larsen, Z. Zheng, and R.A. Couture, Colloid formation at waste plume fronts. Environ. Sci. Technol. 38, 6066–6073, 2004. Berkeley Lab Report LBNL-56059.

Zheng, Z., J. Wan, and T.K. Tokunaga, Sodium meta-autunite colloids: Synthesis, characterization, and stability. J. Colloid Interface Sci. (in review), 2005. Berkeley Lab Report LBNL-54563.

Wan, J., Z. Zheng, and T.K. Tokunaga, Natural abundance and mobile fractions of nanoparticles in soils. (Manuscript in Preparation, 2005).

ACKNOWLEDGMENTS

As(V) Sorption on Hematite:
Complexation Geometry Obtained from Combined Surface X-Ray Diffraction and Grazing-Incidence X-Ray Absorption Spectroscopy

Glenn Waychunas, Tom Trainor[1], Peter Eng[2], James Davis[3], and John Bargar[4]

[1]**University of Alaska, Fairbanks,** [2]**University of Chicago**

[3]**U.S. Geological Survey, Menlo Park ,** [4]**Stanford Synchrotron Radiation Laboratory**

Contact: Glenn Waychunas, 510/495-2224. GAWaychunas@lbl.gov

RESEARCH OBJECTIVES

The objectives of this work were to combine surface x-ray diffraction results of wet hematite surfaces, with arsenate complexation structure derived from surface extended x-ray absorption fine structure (EXAFS) measurements. Using these two techniques together, it is now possible to describe the geometry of sorbed metal complexes with unrivaled detail. This enables testing of both structural and thermodynamic models for sorption and surface complexation, and direct comparisons with molecular-dynamics (MD) simulations of surface reactions.

APPROACH

Surface diffraction of the wet hematite (0001) and (1–102) surfaces can be done using crystal truncation rod (CTR) measurements to obtain the reconstructed or relaxed configuration of surface ions. This has been done (Trainor et al., 2005) and shows that the wet hematite surface is highly defective, with iron atoms missing from the double layers that characterize the bulk structure. The missing atoms are those that would ordinarily share FeO_6 polyhedral faces with one another. We then obtained polarized EXAFS structure functions for arsenate sorbed on the wet (0001) and (1-102) hematite surfaces at SSRL beamline 11-2, and used the hematite surface structure to interpret the results.

ACCOMPLISHMENTS

The results show details of surface complexation that could not have been recovered without these methods (Figure 1). In particular, there is an abundance of "edge-sharing" arsenate-FeO_6 units on the surface, which results from the high proportion of available edge-sharing sites, but relative scarcity of adjacent FeO_6 units allowing "corner-sharing" arsenate attachment. The measurements also

Figure 1. Cartoon showing two views of arsenate complexes (green tetrahedral) as they could sorb on a wet hematite (0001) surface. Of these types, only the edge-sharing bidentate complex is actually observed. Note that the hematite surface is only partially populated by FeO_6 unit (red octahedral) as indicated by CTR work.

demonstrated self-consistency of the hematite surface structure model, and thus helped to verify the CTR diffraction work. We also determined that the method could be applied to complexation coverages as low as about 5% of one monolayer.

SIGNIFICANCE OF FINDINGS

The results indicate the powerful nature of such combined surface probes of interfacial reactions. Prior to this type of study, the surface structure information would not have been accurate enough to derive a proper model of the complexation. We can now proceed to develop MD simulations of surface reactions with a detailed knowledge of the expected complexation geometries. This work is continuing with other surface sorbants, including silicate, phosphate, and selenate, and the CTR work is being extended to include refinements with sorbates present on the scattering surfaces.

RELATED PUBLICATIONS

Trainor, T., P. Eng, G.E. Brown, G. Waychunas, M. Newville, S. Sutton, and M. Rivers, Structure and reactivity of the hydrated hematite (0001) surface. Surface Science, 573, 204–224, 2005.

Waychunas, GA, T. Trainor, P. Eng, J. Catalano, G.E. Brown, J. Rogers, and J. Bargar, Surface complexation studied via combined grazing-incidence EXAFS and surface diffraction: Arsenate on hematite. Anal. Bioanal. Chem. (in press), 2005.

ACKNOWLEDGMENTS

http://www-esd.lbl.gov/